APPLICATIONS OF ON-LINE MULTIDIMENSIONAL CHROMATOGRAPHY TO SOLVENT REFINED COAL

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Solvent refined coal (SRC) is predominately aromatic in nature and contains many polyaromatic hydrocarbons (PAHs). Several PAH's are highly carcinogenic and therefore a knowledge of PAH distribution in SRC is important for health reasons as well as the basic information about the composition of SRC.

SRC is a complex mixture and attempts to elucidate structure or compositional details by a single analytical technique have had limited success. We have chosen several on-line multidimensional chromatographic techniques to examine the hexane soluble fraction of SRC. These techniques include LC (silica gel)/ LC (reverse phase); LC/GC; and LC/LC/Fluorescence. The latter technique proved to be the most useful and will be discussed in detail in this paper.

An SRC sample from AMAX feed stock (obtained from Southern Services, Inc., Wilsonville, Ala) was continously extracted with hexane.

A prepacked silica gel column (size A; 24 x 1 cm; S1-60 silica gel) from E. M. Laboratories, Cinn. Ohio was the first column. HPLC grade hexane, 1.8 ml/min was used to elute a 250 microliter solution of approximately 50 mg of sample. Typical results are shown in figure 1. Note in figure 1 that it was necessary to backflush the column after 70 minutes to elute high molecular weight material. The column was also washed with methylene chloride for 30 minutes before another sample was injected. The fractions containing PAHs are numbered 5 to 10.

Silica gel separates PAH's roughly by the number of condensed aromatic rings. Six fractions of potential PAH content wer chosen based on the retention times of a standard sample containing: Napthalene, 1-Methylnaphthalene, 2-Methylnaphthalene, Acenaphthalene, Flurene, Phenanthrene, Anthracene, 2-Methylanthracene, Fluorathene, Pyrene, Benzo(A)Anthracene, Chrysene, Fluoranthene, Perylene, Benzo(A)Pyrene, Benzo(G,H,I)Perylene, Indeno(1,2,3)Pyrene.

In early work the six fractions were collected manually, dried by nitrogen, dissolved in acetonitrile and injected onto an analytical reverse phase column, Vydac RP Column, 25x0.32 cm (Separations Group, Hisperia Ca.). Mobile phase was a mixture of acetonitrile and water (composition and flow rate changed for different fractions). Detection was a UV-254 nm photometer coupled in series with a Spectrofluorometer (Varian Model SF-330, Palo Alto, CA) equipped with a 16 ul HPLC flow cell.

PAH's were identified by 3 chromatographic techniques: (1) rentention time; (2) ratio of fluorescence/UV detector response; (3) fluorescence spectrum of trapped fractions in the SF 330 flow cell.

PAH distribution in the fractions is shown in Table 1. Characterization by simple retention time, and fluorescence/UV response ratios was difficult. Figures 2,3,4 show fraction 7 eluted under identical chromatographic conditions, but recorded at 3 separate fluorescence excitation and emission wavelengths. The selective fluorescence response of the various PAH's was the key to identification. Note that standard samples are shown under the SRC samples in Figures 2, 3 and 4 to aid in identification.

Table 1 PAH Distribution in SRC Fraction

Fraction	PAH
5	napthalene, 2-methylnaphthalene
6	naphthalene
7	phenanthrene, anthracene, 2-methylanthracene and pyrene
8	fluoranthene
9	benzo (a) anthracene, perylene and benz (a) pyrene
10	benzo (a) anthracene, perylene and benz (a) pyrene

INSTRUMENTATION

Figure 5 is a schematic of the multidimensional or LC/LC/Fluorescence system. The LC is a Varian model 5040, a single reciprocating piston pump with 3 solvent inlet valves controlled by a microprocessor. For LC/LC operation two Valco automatic six-port valves are used to trap fractions and divert the proper fraction to the second LC column. One limitation of the on-line LC/LC system is the incompability of solvent for the different LC columns. Small volumes of hexane (10-30 ul) such as used here can be injected onto the reverse phase system.

The LC/GC system used employed a Varian model 8070 LC/GC interface and has been reported by Apffel elsewhere (1). In this application a hydrocarbon group separation was performed by HPLC on a 5 μ silica column using hexane as a mobile phase (See figure 6). The PAH's were sampled at points determined by standards and automatically injected into a capillary GC. The GC separation was temperature programmed and run on either an SE-30 or a SE-52 WCOT capillary. GC detection was by FID (See Figure 7).

CONCLUSIONS

On-line coupled chromatographic techniques allow separations not easily done off-line. The on-line techniques are easily automated (increasing reproducibility) and allow small transfer volumes between systems. The main limitation with LC/LC is the incompatibility of mobile phases when the columns are normal phase and reverse phase. With LC/GC the main problem is quantitation (since only a portion of the peak is injected) and degradation of GC columns with some LC mobile phases. The use of selective detectors in series is a good technique to examine complex fractions like SRC and enhances the separating power.

REFERENCES

(1) A. Apffel, R. Majors, H. McNair, "Quantitative Studies Using an LC/GC System"; paper presented at Pittsburgh Conference March 1980; submitted to J. Chromatography Science.

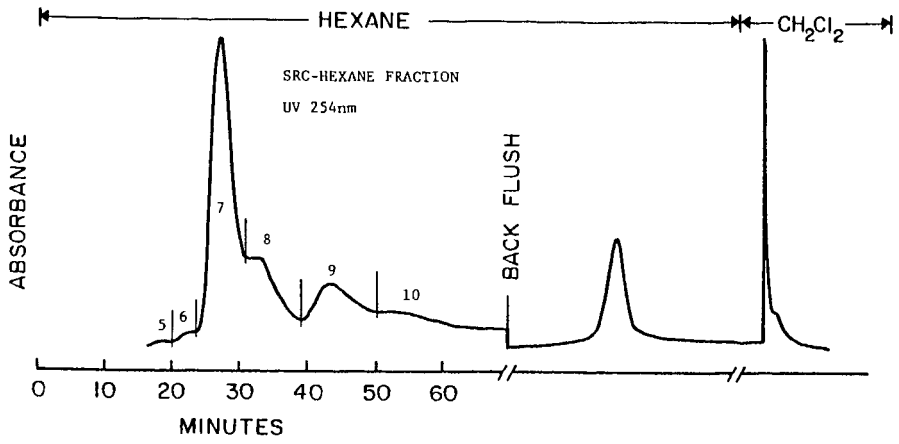

Fig. 1 Fraction of SRC from LC Analysis for Further Work

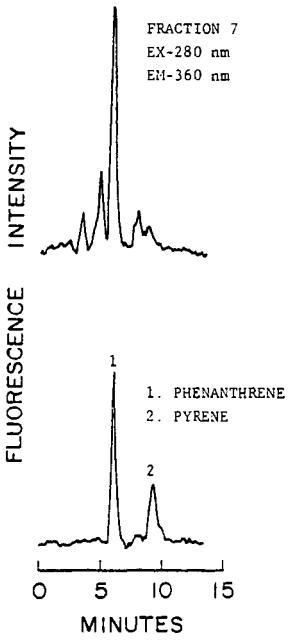

Fig. 2 Fraction 7

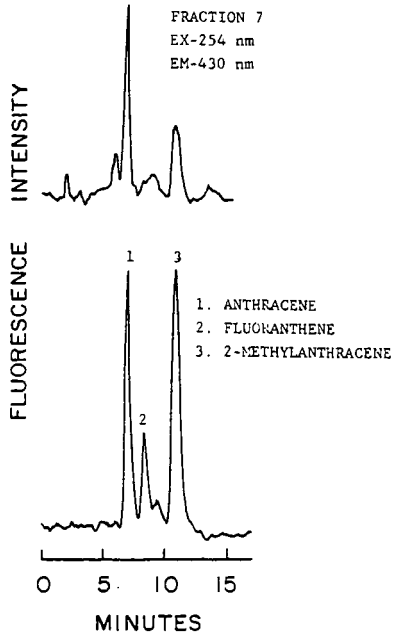

Fig. 3 Fraction 7

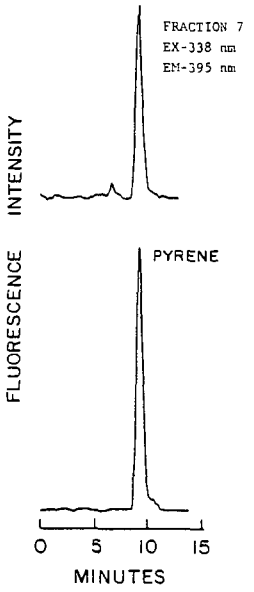

Fig. 4 Fraction 7

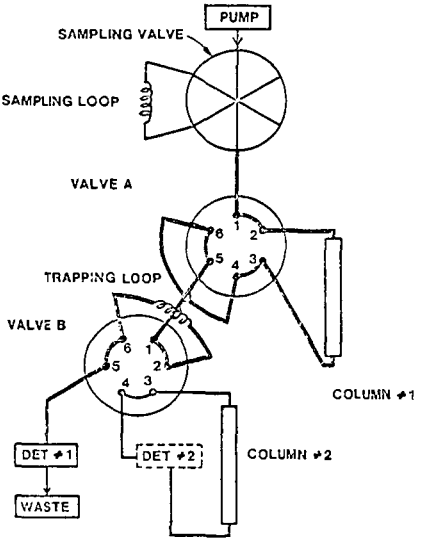

Fig. 5 Column Switching Schematic-LC/LC/Fluorescence

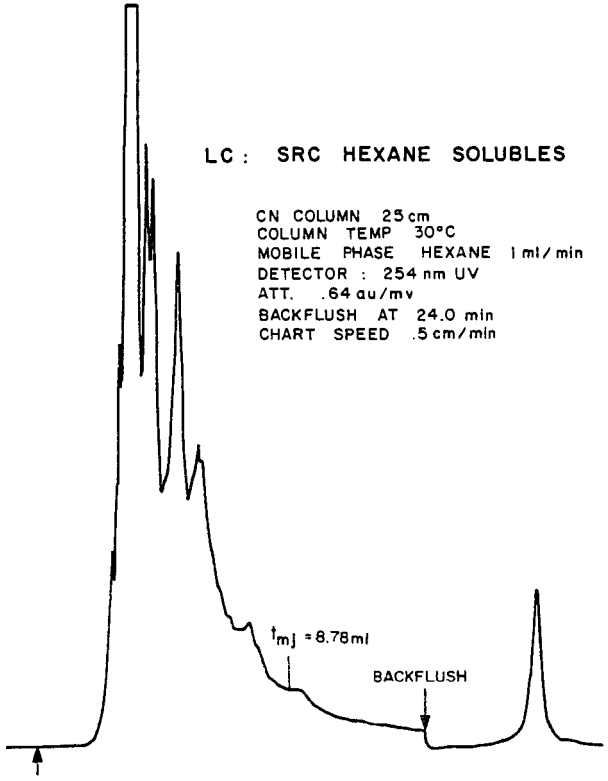

Fig. 6 LC Trace of Hexane Soluble Fraction of SRC

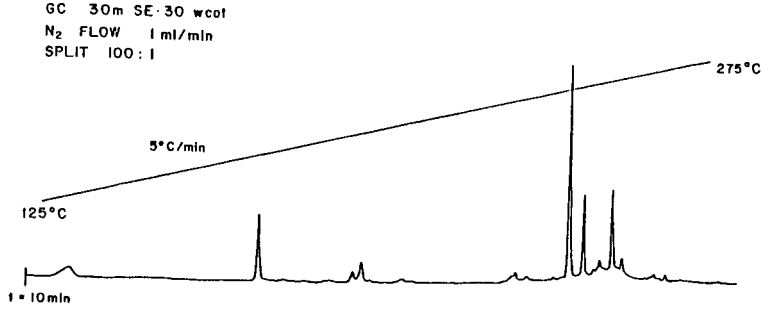

Fig. 7 Analysis of PNA Fraction From LC